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THERMODYNAMICS OF THE PYROLYSIS OF HYDROCARBONS
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In the process of the pyrolysis of hydrocarbons in a nitrogen plasma, a number of valuable products--acetylene, hydrogen cyanide, cyanide and carbon black--are obtained. Ethylene, homologs of acetylene, amines and others are formed in small amounts.

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The possibility of obtaining combined nitrogen in the form of hydrogen cyanide in the temperature range of 2000-3500°K is indicated in the literature [1-4].

Graphite or hydrocarbon (methane, acetylene) was used as the source of carbon in the study [1]. Conducting a thermodynamic calculation of the basic reaction, taking place in the system, the authors established the possibility of obtaining significant concentrations of hydrogen cyanide under high-temperature conditions.

Reference [2] is dedicated to finding the optimal conditions for conducting the process, under which the maximum concentration of HCN is obtained. Using the thermodynamic calculation, the authors determined that under a pressure of 1000-4000 atm and a temperature of 4000°K, the yield of hydrogen cyanide attains 30%.

In references [3, 4] it is reported that in converting hydrocarbons in a nitrogen plasma, the hydrogen cyanide is formed together with significant amounts of acetylene.

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*Numbers in right hand margin indicate pagination in the foreign text.

EQUILIBRIUM CONSTANTS OF THE SYSTEM H-C-N

Substance	Constants	Temperature, °K							
		1000	2000	2500	3000	3100	3200	4000	5000
H ₂	K ₁	1.961 · 10 ¹⁷	3.816 · 10 ⁵	1.597 · 10 ³	4.050 · 10 ¹	2.235 · 10	1.278 · 10	3.977 · 10 ⁻¹	2.443 · 10 ⁻²
C*	p _c	6.458 · 10 ⁻³⁰	3.430 · 10 ⁻¹¹	1.836 · 10 ⁻⁷	5.506 · 10 ⁻⁵	1.379 · 10 ⁻⁴	3.259 · 10 ⁻⁴	6.619 · 10 ⁻²	4.501
C ₂	K ₃	1.760 · 10 ²⁵	2.532 · 10 ⁹	1.658 · 10 ⁶	1.237 · 10 ⁴	5.615 · 10 ³	2.675 · 10 ³	2.686 · 10 ¹	6.719 · 10 ⁻¹
C ₃	K ₄	3.558 · 10 ⁵⁸	9.486 · 10 ²⁰	7.068 · 10 ¹³	1.238 · 10 ⁹	2.113 · 10 ⁸	4.027 · 10 ⁷	1.366 · 10 ³	3.609 · 10 ⁻¹
N ₂	K ₅	1.163 · 10 ⁴³	1.251 · 10 ¹⁸	1.192 · 10 ¹³	5.248 · 10 ⁹	1.506 · 10 ⁹	4.469 · 10 ⁸	3.228 · 10 ³	9.255 · 10 ²
CH	K ₆	4.944 · 10 ¹²	3.588 · 10 ³	5.002 · 10	2.844	1.786	1.156	7.667 · 10 ⁻²	8.606 · 10 ⁻³
CH ₂	K ₇	2.018 · 10 ³⁴	7.995 · 10 ¹⁰	1.537 · 10 ⁶	1.081 · 10 ³	3.346 · 10 ²	1.114 · 10 ²	1.203 · 10 ⁻¹	5.006 · 10 ⁻⁴
CH ₃	K ₈	2.076 · 10 ⁴⁷	1.949 · 10 ¹⁴	4.229 · 10 ⁷	1.480 · 10 ³	2.821 · 10 ²	5.962 · 10	3.825 · 10 ⁻³	1.651 · 10 ⁻⁶
CH ₄	K ₉	6.056 · 10 ⁸²	1.727 · 10 ¹⁸	1.854 · 10 ⁹	1.898 · 10 ³	2.049 · 10 ²	2.542 · 10	6.046 · 10 ⁻⁵	1.903 · 10 ⁻⁹
C ₂ H	K ₁₀	2.500 · 10 ⁴⁸	5.148 · 10 ¹⁷	3.528 · 10 ¹¹	2.698 · 10 ⁷	5.837 · 10 ⁶	1.390 · 10 ⁶	1.873 · 10 ²	1.464 · 10 ⁻¹
C ₂ H ₂	K ₁₁	7.180 · 10 ⁶⁶	3.568 · 10 ²³	7.698 · 10 ¹⁴	1.275 · 10 ⁹	1.486 · 10 ⁸	1.980 · 10 ⁷	7.261 · 10	3.100 · 10 ⁻³
C ₂ H ₄	K ₁₂	6.277 · 10 ⁹⁶	7.298 · 10 ²⁶	6.732 · 10 ¹⁴	6.311 · 10 ⁶	3.198 · 10 ⁵	1.954 · 10 ⁴	5.805 · 10 ⁻⁴	5.546 · 10 ⁻¹⁰
C ₃ H	K ₁₃	4.786 · 10 ⁷⁶	1.333 · 10 ²⁸	1.395 · 10 ¹⁸	5.754 · 10 ¹¹	6.266 · 10 ¹⁰	6.546 · 10 ⁹	4.160 · 10 ³	2.082 · 10 ⁻¹
C ₄ H	K ₁₄	2.483 · 10 ¹⁰¹	9.100 · 10 ³⁶	1.420 · 10 ²⁴	5.023 · 10 ¹⁵	2.056 · 10 ¹⁴	1.309 · 10 ¹³	9.090 · 10 ⁴	1.581 · 10 ⁻⁶
C ₄ H ₂	K ₁₅	3.371 · 10 ¹¹⁵	3.333 · 10 ⁴⁰	3.397 · 10 ²⁵	3.404 · 10 ¹⁵	9.268 · 10 ¹⁴	2.401 · 10 ¹²	1.333 · 10 ⁻³	4.015 · 10 ⁻¹³
NH	K ₁₆	3.062 · 10 ¹³	1.034 · 10 ⁴	1.232 · 10 ²	6.333	3.917	2.497	1.522 · 10 ⁻¹	1.614 · 10 ⁻²
NH ₂	K ₁₇	5.025 · 10 ²⁷	9.393 · 10 ⁷	9.363 · 10 ³	1.945 · 10	7.163	2.806	8.250 · 10 ⁻³	7.593 · 10 ⁻⁵
NH ₃	K ₁₈	1.805 · 10 ⁴⁴	5.538 · 10 ¹²	2.421 · 10 ⁶	1.363 · 10 ²	2.810 · 10	6.396	6.609 · 10 ⁻⁴	4.346 · 10 ⁻⁷
CN	K ₁₉	4.492 · 10 ³⁶	1.186 · 10 ¹⁵	5.448 · 10 ¹⁰	6.923 · 10 ⁷	2.361 · 10 ⁷	8.606 · 10 ⁶	1.659 · 10 ⁴	1.118 · 10 ²
C ₂ N ₂	K ₂₀	3.516 · 10 ³⁷	1.846 · 10 ³³	2.547 · 10 ²²	1.469 · 10 ¹⁵	9.993 · 10 ¹³	8.037 · 10 ¹²	1.314 · 10 ⁶	4.837
HCN	K ₂₁	3.087 · 10 ³⁴	4.846 · 10 ²⁰	7.964 · 10 ¹³	2.361 · 10 ⁹	4.391 · 10 ⁸	9.065 · 10 ⁷	5.111 · 10 ³	2.021

*The value of the carbon vapor pressure is given in the table.

Thus, the pyrolysis of hydrocarbons in a nitrogen plasma is of interest as one of the direct methods of obtaining acetylene and combined nitrogen.

In order to obtain more reliable data on the thermodynamics of the process of the pyrolysis of hydrocarbons in a nitrogen plasma and an analysis of the optimal conditions for obtaining the maximum yield of C_2H_2 and HCN, we made a thermodynamic analysis of the system H-C-N.

The influence of temperature within the range 1000-5000°K, the influence of pressure and the composition of original components on the partial pressures of the substances were revealed in the process of the investigation.

The calculations considered the molecules, atoms and radicals, the partial pressures of which in the case of equilibrium may have a value of more than 10^{-3} atm: C, C_2 , C_3 , N, N_2 , H, H_2 , CH, CH_2 , CH_3 , CH_4 , C_2H , C_2H_2 , C_2H_4 , C_3H , C_4H , C_4H_2 , NH, NH_2 , NH_3 , CN, C_2N_2 , HCN. As preliminary calculations showed, the degree of ionization of the gas in the conditions investigated is small, the concentration of electrons is less than $10^{-4}\%$, due to which these factors need not be considered in the process of calculation.

Thus in making the calculations, we proceeded under the assumption that solid carbon is significantly less susceptible to reaction than gaseous carbon in that reactions take place in the gas phase, in the condition of chemical equilibrium for all substances participating in the reaction, may be given in the form of the equation:

$$K_i = \frac{p_i}{p_C^b p_N^c p_H^d}, \quad (1)$$

where K_i is the equilibrium constant of the synthesis reaction of the i -th rank substance from the elements C, N, H; p_C , p_N , p_H are

the partial pressures of the elements; b, c, d, r are the stoichiometric coefficients of the components participating in the reaction.

The values of the equilibrium constants, which we calculated according to the data of the literature [6, 7] are given in the table.

Under pressures close to atmospheric pressure, real gases are satisfactorily subject to the ideal gas laws. Then the value of total pressure and the conditions of material balance are written in the form:

$$\left. \begin{aligned} \Sigma p_i &= P; \\ \frac{\Sigma C}{\Sigma H} &= R; \\ \frac{\Sigma H}{\Sigma N} &= S; \end{aligned} \right\} \begin{array}{l} (2) \\ (3) \\ (4) \end{array}$$

where P is the total pressure of the system, atm; and R, S, are the ratio of elements in the original substances.

By means of simple algebraic transformations the values of Σp_i , ΣC , ΣH , ΣN are expressed with the use of the three unknowns p_C , p_H and p_N . In this way, a system of three equations with three unknowns is obtained. The system is solved by means of successive approximations with the use of the "Minsk-22" computer. Algorithms of successive approximations were determined for each temperature range.

The condensation of carbon in the solid phase under atmospheric pressure and with the ratio of initial components C : H : N = 1 : 4 : 1 begins at temperatures below $T_K \simeq 3150^\circ K$. In this case equation (3) is not satisfied.

Figure 1 presents data characterizing the dependence of the equilibrium partial pressures of the basic products of the reaction

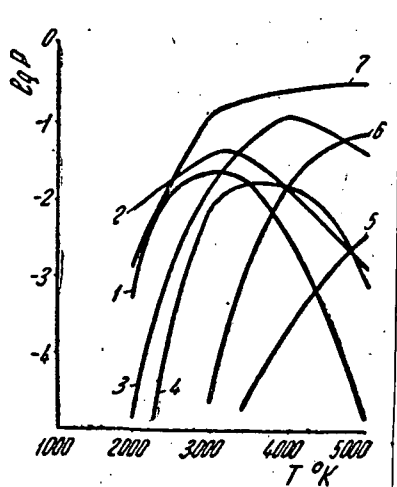


Fig. 1. Dependence of equilibrium partial pressure of the reaction products on temperature. (1) acetylene; (2) hydrogen cyanide; (3) cyanide; (4) ethynyl; (5) atomic nitrogen; (6) carbon; (7) monoatomic hydrogen.

(C_2H_2 , HCN, CN, C_2H) on temperature at a pressure of one atmosphere, when methane served as the carbon source, and the ratio between the components was $C : H : N = 1 : 4 : 1$.

The maximum values obtained $p_{C_2H_2}$ and p_{HCN} are reached close to the point of carbon condensation. The maxima of the partial pressures of cyanide (CN) and ethylene (C_2H) are displaced toward high temperatures. At temperatures on the order of $4000^\circ K$ it is possible to expect an increased yield of cyanide compounds due to the increase in the partial pressure of CN; at $4000^\circ K$, $p_{CN} = 0.1086$ atm.

At $2000^\circ K$, hydrogen is dissociated to a significant degree; an analogous condition for nitrogen begins only at temperatures exceeding $4500^\circ K$. The maximum partial pressures of the radicals C_3H and C_4H are observed in the temperature range of 3500 – $4000^\circ K$ and are $0.219 \cdot 10^{-1}$ and $0.394 \cdot 10^{-2}$ atm, respectively. The partial vapor pressures of the remaining substances do not exceed 10^{-4} atm. In the temperature range above $4500^\circ K$, an intense dissociation of all molecules contained in the system begins.

Investigations of the process of pyrolysis in argon and hydrogen plasma [5] showed the formation time of solid carbon exceeds the time of the gas phase reactions, having a duration on the order of 10^{-3} , 10^{-4} sec. Plasma technology permits products to be frozen out, obtained in the equilibrium state, at practically any predetermined reaction time. In this case, it is expedient for temperatures which are less than the temperature of carbon condensation

to determine the quasi-equilibrium partial pressures of the substances with regard to the fact that all the carbon is found in the gas phase. The given calculations agree well with the results of the experiments.

Results of a calculation of the quasi-equilibrium partial pressures of the substances for the system H-C-N are given below.

Figure 2 presents the results of an investigation of the influence of the hydrogen content in the system on the quasi-equilibrium partial pressures of substances. The solid lines indicate

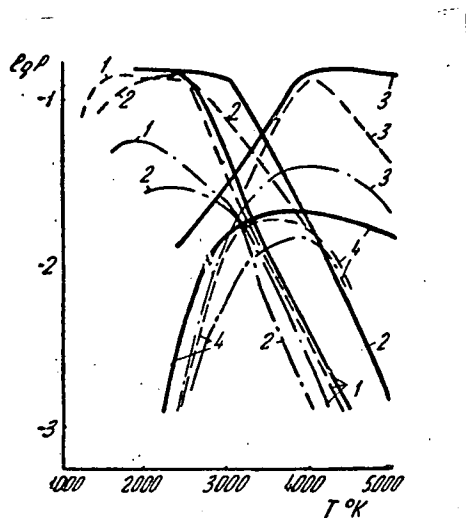


Fig. 2. Influence of the ratio C : H on the quasi-equilibrium partial pressures of the substances (C : N = 1 : 1). (1) acetylene; (2) hydrogen cyanide; (3) cyanide; (4) ethylene.

the pressures of the substances, given the ratio C : H : N = 1 : 1 : 1; the dotted lines indicate the ratio C : H : N = 1 : 4 : 1. In this case methane is used as the carbon source.

The dot-dash lines correspond to the case of obtaining cyanide compounds from methane and ammonia given a ratio C : H : N = 1 : 7 : 1.

The optimum yield of hydrogen cyanide and acetylene (22.1% by vol. C_2H_2 and 20.6% by vol. HCN) can be obtained using hydrocarbons rich in carbon as a raw material. The use of methane leads to a decrease in the yield of acetylene and hydrogen

cyanide by 13.9 and 10.7%, respectively. Using ammonia as the nitrogen source leads to a decrease in the yield of acetylene and hydrogen cyanide ($C_{C_2H_2} = 8.79\%$ by vol. and $C_{HCN} = 6.55\%$ by vol.). The partial pressures of these substances are reached in the temperature range of 1600-2500°K.

An increase in the yield of cyanide compounds and acetylene may be expected at a temperature of approximately 4000°K due to the increase in the partial pressures of the radicals CN and C_2H . Diluting the mixture with hydrogen leads to a decrease in the partial pressures of these radicals.

The partial pressures of the radicals C_3H and C_4H reach values of $0.655 \cdot 10^{-1}$ atm and $0.689 \cdot 10^{-1}$ atm for mixtures rich in carbon at temperatures of 3000-3500°K.

An increase in the amount of hydrogen leads to a decrease in the partial pressures of the radicals.

With a ratio of C : H : N = 1 : 1 : 1 in the temperature range 2500-3500°K, the partial pressures of dicyanide C_2N_2 and the radical C_4H_2 are $0.165 \cdot 10^{-2}$ atm and $0.39 \cdot 10^{-1}$ atm, respectively.

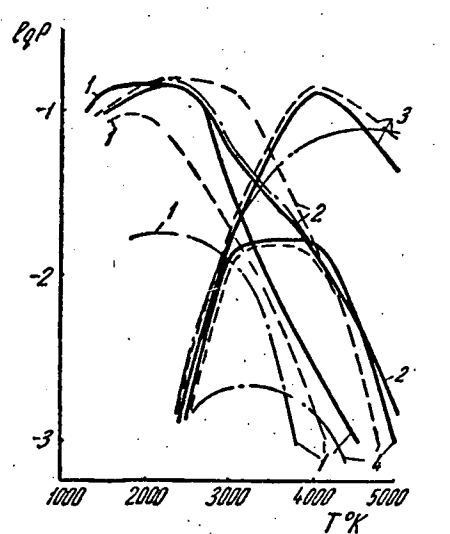


Fig. 3. The influence of the ratio C : N on the quasi-equilibrium pressures of the substances (C : H = 1 : 4). (1) acetylene; (2) hydrogen cyanide; (3) cyanide; (4) ethylene.

Figure 3 shows the influence of an excess of nitrogen on the yield of basic reaction products. In this case, methane is the source of the carbon and hydrogen. The partial pressures of cyanide compounds increase with a two-fold excess of nitrogen (C : H : N = 1 : 4 : 2) and reach $P_{HCN} = 0.123$ atm, $P_{C_2H_2} = 0.136$ atm; the partial pressures of acetylene and ethylene dropped; also the partial pressures of secondary reaction products decreased.

These data enable us to select the optimal technological conditions for the process (temperature, pressure) and the initial source, depending on which of the products is sought. If pyrolysis of hydrocarbon takes place for the purpose of obtaining acetylene, then it is

worthwhile to select mixtures rich in carbon with a ratio $C : N = 1 : 1$.

In the case of using hydrogen cyanide as the basic product, the optimum yield is obtained with a two-fold excess of nitrogen. An increase in the temperature to approximately 4000°K also leads to an increase in the yield of cyanide compounds. With temperatures of around 4000°K it is possible to obtain a gas containing practically only cyanide compounds.

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According to the calculations of American investigators [2], the increase in pressure leads to an increase in the yield of cyanide compounds.

We investigated the influence of the total pressures in the system on the pyrolysis of methane with a ratio of $C : H : N = 1 : 4 : 1$ in the range of 0.1-30 atm. In Figure 4 the solid lines indicate the value of the quasi-equilibrium partial pressures of

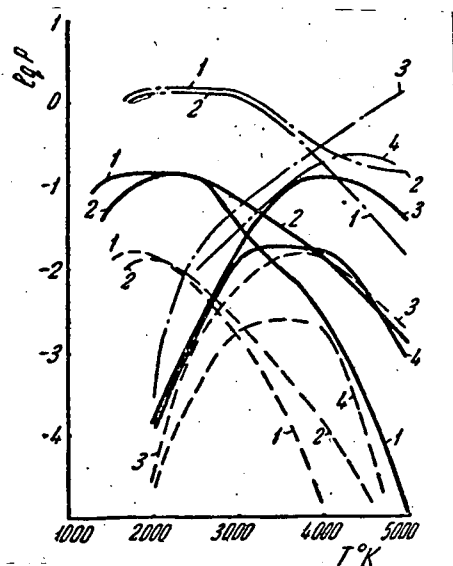


Fig. 4. Influence of pressure on the quasi-equilibrium state of substances. (1) acetylene; (2) hydrogen cyanide; (3) cyanide; (4) ethylene.

the basic reaction products with a pressure in the system equal to 1 atm, and the dotted lines indicate 0.1 atm while the dash-dot lines indicate 10 atm. Increase in pressure displaces the maximum yield of HCN toward the highest temperature; the relative concentrations of acetylene and hydrogen cyanide in this case change insignificantly. The process takes place under an electrical discharge which allows for an improvement in the sanitary-hygienic working conditions. Moreover, with a decrease in pressure the optimal temperature of the process also decreases, and consequently, there is a decrease in

the energy consumption per unit of production.

It is important to note that energy consumption upon obtaining acetylene by means of pyrolysis of hydrocarbons in nitrogen plasma is close to the energy consumption of the analogous process in hydrogen plasma. Figure 5 shows the dependence of the specific energy consumption on the mean mass temperature of the pyrolysis reaction of methane with $C : H : N = 1 : 4 : 1$.

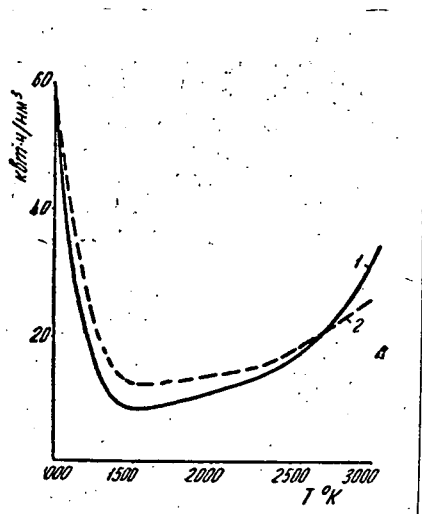


Fig. 5. Specific energy consumptions in case of the pyrolysis of methane in a nitrogen plasma. (1) for 1 nm³ acetylene; (2) for 1 nm³ hydrogen cyanide.

Curve 1 characterizes the energy consumption for 1 nm³ of acetylene, whereby electrical energy is not consumed for obtaining hydrogen cyanide. Curve 2 shows the energy consumption for 1 nm³ HCN under the condition that electrical energy is not consumed for obtaining acetylene.

In calculating the energy consumption, the efficiency of plasma reactors and the reagents were not considered.

The complex conversion of hydrocarbon gases in plasma with the liberation of hydrogen cyanide, acetylene and

homologs of acetylene enables one to significantly improve the economic indicators of this process.

The results of the thermodynamic calculation provide the basis for drawing certain conclusions about the kinetics of this process. First of all, it is obvious that the process of pyrolysis must be conducted under conditions of a quasi-equilibrium state, in order for the reaction time to be less than the condensation time of carbon from the gas phase; i.e. with $\tau < 10^{-2}$ sec. /24

The second important characteristic of the process is the metastability of the reaction products of hydrogen cyanide and

acetylene at room temperature. The products of the reaction must be rapidly chilled in order to preserve them. The rate of chilling must be within the bounds of 10^7 - 10^8 °/sec. It may be obtained by various methods: with cooling the gases by means of pumping liquid hydrocarbons into the gas flow; recirculation of cooled gases; expansion of gases in a Laval nozzle; in a fluidized bed of solid particles, etc.

In the case of cooling the products of pyrolysis, secondary reactions occur. Thus as in the case of methane pyrolysis in a hydrogen gas, it is necessary to expect that ethynyl C_2H will react with the hydrogen, forming acetylene. The radicals CH , CH_2 and CH_3 are characterized by a good reaction capacity; they may enter the reaction with hydrogen, forming methane. The reactions of the radicals C_3H , C_4H and C_4H_2 with hydrogen lead to the formation of homologs of acetylene, and so forth.

CONCLUSIONS

1. A thermodynamic calculation of the process of converting hydrocarbon in a nitrogen plasma in the temperature range of 1000-5000°K is made. It is established that the process must be conducted under quasi-equilibrium conditions, when the reaction time is less than the condensation time of carbon. In this case it is possible to obtain a high yield of acetylene and hydrogen cyanide in the temperature range of 1500-2500°K.

With an increase in temperature to 4500°K, the concentration of cyanide compounds increases due to the increase of the partial pressure of the radical CN .

2. The maximum concentration of cyanide compounds and acetylene are obtained in the case where mixtures rich in carbon are used as a raw material. With pyrolysis is performed for the purpose of obtaining hydrogen cyanide; the reaction must be conducted

with an excess of nitrogen and at a high temperature.

3. In the process studied, specific energy consumptions for 1 nm³ acetylene do not greatly exceed the energy consumptions for the pyrolysis process of methane in a flow of hydrogen plasma.

In this case, hydrogen cyanide is obtained as a secondary product free of charge.

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